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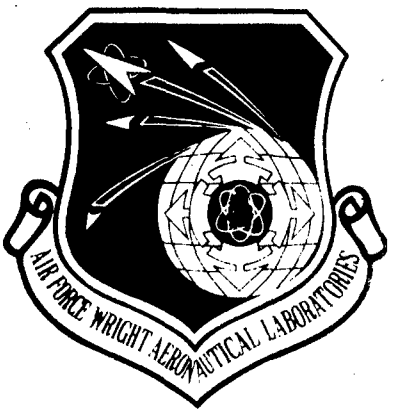

NEW ACETYLENE-TERMINATED QUINOXALINE OLIGOMERS

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A series of acetylene-terminated quinoxaline oligomers have been synthesized by methods for using a minimum amount of tetraamine, the most expensive component in the system. Samples of the oligomers have been furnished to the Materials Laboratory for further study.

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FOREWORD

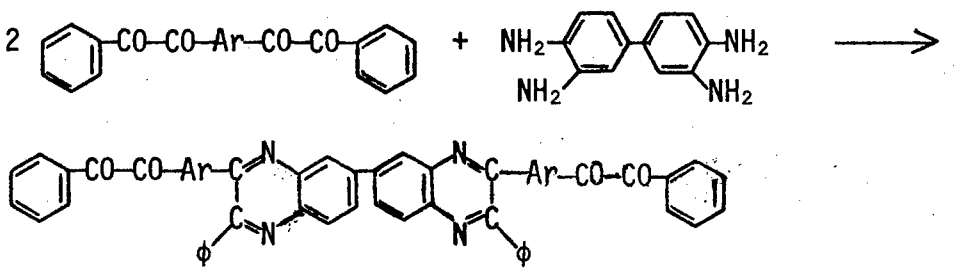
This report was prepared under the Contract No. F33615-80-K-5166 administered by Dr. F. L. Hedberg, Materials Laboratory, Air Force Wright Aeronautical Laboratories. Dr. Hedberg was the project scientist.

The report covers work performed from August 15, 1980 to November 14, 1981.

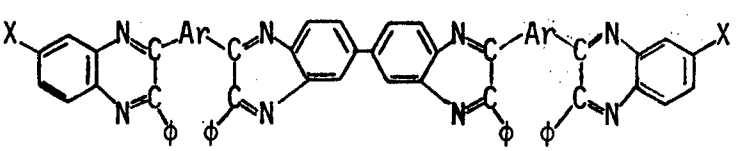
INTRODUCTION

Quinoxaline polymers have been found to be excellent adhesives for use in the airplane industry, but they are still extremely expensive. The Materials Laboratory at Wright-Patterson Air Force Base has arranged for us to seek ways of making these more economically, especially with the use of the minimum amount of the tetraamine, which is the most expensive ingredient. We have previously been able to improve the synthesis of the bisglyoxals needed for these adhesives,[1] and are now seeking to obtain the oligomeric quinoxaline polymers with acetylene end groups which we believe can be cured in place to give good adhesives.

The general method of synthesis which have been developed is to first condense the quinoxaline oligomer with glyoxal end groups.

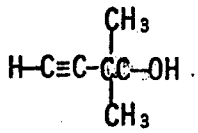


The oligomer is then condensed with a diaminobenzene derivative which has a substituent in it which can be converted to an acetylene to obtain the oligomer.

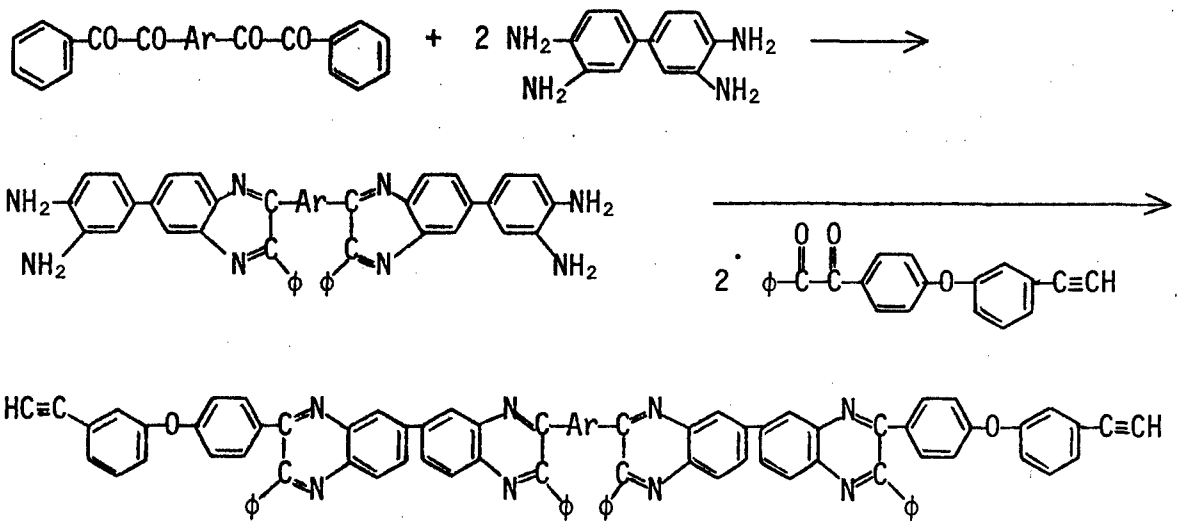


I

Finally the X group in this oligomer is converted to an acetylene end group by an appropriate method. Sometimes we have used bromo-3,4-diaminobenzene directly, and then have replaced the halogen atom in this group with



This group can be converted to the acetylene by loss of acetone. One of the end-capping reagents, 4-(3-ethynylphenoxy)benzil was synthesized by the nucleophilic displacement of the nitro group of p-nitrobenzil by treatment with the sodium 3-ethynylphenolate.



II

EXPERIMENTAL

4-Nitrodiphenylacetylene. p-Bromonitrobenzene (20.20 g, 0.10 mol), palladium diacetate (0.065 g), triphenylphosphine (1.301 g), copper iodide (0.82 g), and triethylamine (60 ml) (in case of 1-chloro-4-nitro benzene as starting material, diisopropylamine was used as solvent) were stirred at reflux temperature under nitrogen. Phenyl acetylene (20.43 g, 0.20 mol) was added and rinsed down with triethylamine (10 ml). The reaction mixture was

stirred at reflux temperature for 24 hr. The reaction mixture was poured into dilute HCl solution. The solid product was washed successively with water and methanol. After drying, the yield of 4-nitrodiphenylacetylene was 21.66 g (97%), m.p. 118-119°C (lit.[2], 119-120°C). In case of 1-chloro-4-nitrobenzene as starting material, the yield of 4-nitrodiphenylacetylene was 43%.

4-(3-Bromophenoxy)benzil. This compound was prepared from two routes: (1) m-Bromophenol (9.51 g, 0.055 mol), potassium carbonate (15.18 g, 0.11 mol), and methyl sulfoxide (DMSO, 100 ml) were stirred at 100°C under nitrogen. p-Nitrobenzil (12.75 g, 0.05 mol) was dissolved in 150 ml of DMSO and this solution was added into it. The resulting mixture was stirred for 2 days at 100°C under nitrogen. DMSO was distilled in high vacuum and the mixture was poured into the separate funnels -- 750 ml of water, 300 ml of ether, and 120 g of sodium chloride. After separation of the organic layer, the aqueous layer was extracted with ether (3 x 50 ml). Ether layers were combined, and washed with 5% KOH (600 ml) and 10% NH_4Cl (600 ml). The resulting solution was dried over $MgSO_4$. After evaporation of ether, the crude was purified by column chromatography (silica gel, 40-140 Mesh, benzene as eluent). Pure 4-(3-bromophenoxy)benzil (16.21 g, 85.1%) was obtained as a pale yellow solid, m.p. 69-71°C.

NMR ($CDCl_3$), δ 6.70-8.02 (m, 13H)

Anal. Calcd. for $C_{20}H_{13}BrO_3$: C, 63.03; H, 3.41; Br, 20.97

Found: C, 62.88; H, 3.50; Br, 20.83.

(2) (4-Phenylethynyl-3'-bromo)diphenyl ether (6.98 g, 0.02 mol) was dissolved in 150 ml of methylene chloride. The flask was suspended in an oil bath maintained at 45°C. Adogen-464 (0.52 g) was added, along with glacial acetic acid (5 ml). Potassium permanganate (4.74 g, 0.03 mol) was added through the

condenser and rinsed down with 150 ml of water. The reaction mixture was refluxed for 24 hr and worked up as described before for the preparation of 1,4-bis(phenylglyoxaloyl)benzene.[1] The crude solid was refluxed in methanol. After cooling, the precipitate was removed by filtration. After evaporation of the supernatant, the crude was purified from column chromatography (silica gel, 40-140 Mesh, benzene as eluent) to afford 2.36 g (31.0%) of pure material, m.p. 69-72°C.

NMR spectra and TLC position were well agreed with the compound prepared from another route (1).

(4-Phenylethynyl-3'-bromo)diphenyl ether. 4-Nitrodiphenylacetylene (4.46 g, 0.02 mol), m-bromophenol (3.46 g, 0.02 mol), and potassium carbonate (anhydrous granular, 13.82 g, 0.10 mol) were mixed with DMSO (40 ml). This reaction mixture was stirred at 80°C oil bath for 30 hr under nitrogen. The resulting mixture was cooled to room temperature and then added to a mixture of 10% HCl (800 ml) and chloroform (200 ml). The organic layer was extracted with six successive 50 ml portions of dilute HCl (to remove all of DMSO), and washed with water, 5% KOH (800 ml) and 10% NH_4Cl (600 ml). The resulting solution was dried over $MgSO_4$. After evaporation of chloroform, the filtrate was recrystallized from benzene-methanol to yield 6.05 g (86.6%) of pure (4-phenylethynyl-3'-bromo)diphenyl ether, m.p. 133.5-134.5°C.

NMR ($CDCl_3$) δ 6.70-8.20 (m, aromatic-H)

Anal. Calcd. for $C_{20}H_{13}BrO$: C, 68.78; H, 3.76; Br, 22.88

Found: C, 67.96; H, 3.91; Br, 22.96.

Acetone adduct of 4-(3-ethynylphenoxy)benzil (EPB). 4-(3-Bromophenoxy)benzil (12.0 g, 31.5 mmol), palladium diacetate (0.0204 g), triphenylphosphine (0.408 g), copper iodide (0.082 g), and dry triethylamine (500 ml) were stirred at reflux temperature under nitrogen. 2-Methyl-3-butyn-2-ol

(5.30 g, 63.1 mmol) was added through the condenser and rinsed down with additional 10 ml of triethyl amine. The reaction mixture was stirred at reflux temperature for 18 hr under nitrogen. After cooling to room temperature, the reaction mixture was poured into a mixture of chloroform (400 ml) and 5% HCl (400 ml). After separation of the organic layer, the chloroform was removed by evaporation. The crude was dissolved in ether (200 ml), and washed with 5% HCl (600 ml), water (200 ml x 3), and saturated NaCl (600 ml). This solution was dried over $MgSO_4$. After evaporation of the ether, the crude was purified by column chromatography (silica gel 40-140 Mesh, benzene as eluent). Pure acetone adduct of EPB (12.10 g, 94.0%) was obtained as a pale yellow solid; m.p. 70-72°C.

NMR ($CDCl_3$), δ 1.73 (d, 6H), 2.20 (s, 1H), 7.0-8.5 (m, 13H)

Anal. Calcd. for $C_{25}H_{20}O_4$: C, 78.14; H, 5.20

Found: C, 77.89; H, 5.19.

(3,4'-Dibromo)diphenyl ether. (1) Sodium hydroxide (1.96 g, 0.049 mol) was dissolved in 30 ml of methanol in 200 ml flask equipped with a mechanical stirrer under nitrogen. m-Bromophenol (8.65 g, 0.050 mol) and dry benzene (50 ml) were added and the mixture was refluxed for 1 hr. The solvent was removed by distillation. When the phenolate salt was cooled, p-dibromobenzene (16.52 g, 0.070 mol) and pyridine (50 ml) was added and dissolved completely. Next, copper iodide (3.81 g) was added and the mixture was stirred at reflux temperature for 16 hr. The resulting mixture was poured into ice water containing HCl and extracted with chloroform. Organic layer was washed with 5% NaOH and saturated NH_4Cl. After evaporation of the chloroform, the distillation in vacuo gave 9.18 g (56.0%) of pure material, a pale yellow liquid, b.p. 140°C (0.2 mm Hg).

NMR ($CDCl_3$), δ 7.0-7.6 (m, aromatic-H)

Anal. Calcd. for $C_{12}H_8Br_2O$: C, 43.94; H, 2.46; Br, 48.72

Found: C, 42.96; H, 2.48; Br, 47.99.

C^{13} NMR also supported this structure.

(2) Potassium hydroxide (2.81 g, 0.05 mol) was poured into 200 ml flask equipped with a mechanical stirrer under nitrogen. m-Bromophenol (8.65 g, 0.05 mol) in 10 ml of toluene was added into it, and the mixture was stirred at 100-115°C for 2 hr until all of the water was removed. p-Dibromobenzene (16.52 g, 0.070 mol), copper iodide (2.38 g), and diglyme (30 ml) were added, and the reaction mixture was stirred at reflux temperature for 24 hr. The resulting mixture was poured into ice water. The aqueous layer was extracted with chloroform. Organic layer was washed with 5% NaOH and saturated NH_4Cl. The distillation in vacuo gave 17.6% yield of pure material.

(3-Phenylethynyl-4'-bromo)diphenyl ether. (3,4'-Dibromo)diphenyl ether (8.20 g, 0.025 mol), palladium diacetate (0.0163 g), triphenylphosphine (0.325 g), copper iodide (0.065 g), and triethylamine (40 ml) were stirred at reflux temperature under nitrogen. Phenylacetylene (2.55 g, 0.025 mol) was added through the condenser and rinsed down with additional 10 ml of triethylamine. The mixture was stirred at reflux temperature for 16 hr under nitrogen. The reaction mixture was poured into a mixture of chloroform (200 ml) and 5% HCl (800 ml). The organic layer was washed with water and saturated NaCl. This solution was dried over $MgSO_4$. After evaporation of chloroform, the crude was purified by column chromatography (silica gel 40-140 Mesh, benzene as eluent). Pure (3-phenylethynyl-4'-bromo)diphenyl ether was obtained as a yellow gum, 8.15 g (93.4%).

NMR ($CDCl_3$) δ 6.90-7.61 (m, Aromatic-H).

Anal. Calcd. for $C_{20}H_{13}BrO$: C, 68.78; H, 3.76; Br, 22.88

Found: C, 67.63; H, 4.07; Br, 23.93.

TLC spot was different from (4-phenylethynyl-3'-bromo)diphenyl ether.

3-(4-Bromophenoxy)benzil. (3-Phenylethynyl-4'-bromo)diphenyl ether (6.98 g, 0.02 mol) was dissolved in 150 ml of methylene chloride. The flask was suspended in a 45°C oil bath. Adogen-464 (0.52 g) was added, along with glacial acetic acid (5.0 ml). Potassium permanganate (4.74 g, 0.03 mol) was added through the condenser and rinsed down with water (150 ml). The reaction mixture was stirred at 45°C oil bath for 16 hr. After cooling to room temperature, the excess potassium permanganate was reduced by adding solid sodium bisulfite. The solution was acidified with concentrated HCl (5 ml), and precipitated manganese dioxide was dissolved by addition of concentrated sodium bisulfite solution. The organic layer was washed with concentrated sodium bicarbonate solution and dried over $MgSO_4$. After evaporation of methylene chloride, the crude was purified by column chromatography (silica gel 40-140 Mesh, benzene as eluent). Pure 3-(4-bromophenoxy)benzil, 6.92 g (90.8%), was obtained as a yellow liquid.

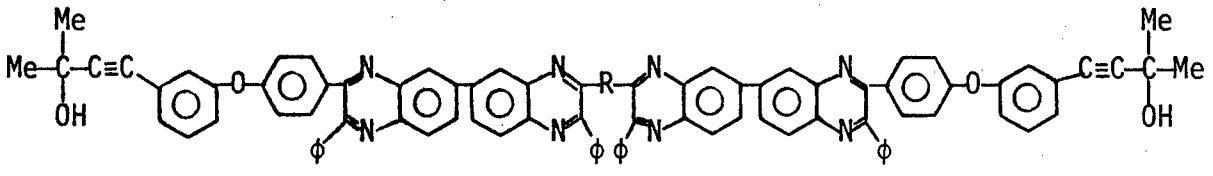
NMR ($CDCl_3$) δ 6.70-8.02 (m, Aromatic-H).

Anal. Calcd. for $C_{20}H_{13}BrO_3$: C, 63.03; H, 3.41; Br, 20.97

Found: C, 62.10; H, 3.75; Br, 21.31.

TLC spot was different to 4-(3-bromophenoxy)benzil.

Acetone adduct of acetylene terminated quinoxaline oligomer. The various structures prepared are shown in Figure 1.



ABATQ

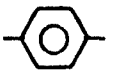
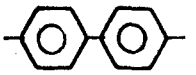
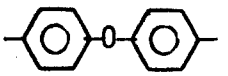
Oligomer	R
ABATQ - 1	
ABATQ - 2	
ABATQ - 3	

FIGURE I. Structures of ABATQ series oligomers

General Preparation

3,3'-Diaminobenzidine (8.0 mmol) was dissolved in m-cresol (10% solution) in 200 ml flask equipped with a mechanical stirrer. The flask was suspended in a 90-100°C oil bath under nitrogen. The 10% m-cresol solution of bis-benzil (4.0 mmol) was added into it and the reaction mixture was stirred for 2 hr at 90-100°C (bath) under nitrogen.

Then, the solution of acetone adduct of EPB (8.8 mmol) in chloroform was added. After removal of the solvent by distillation, the reaction mixture was heated for 2 hr at 90-100°C, and poured into a solution of 10% sodium hydroxide (sufficient quantity to neutralize the m-cresol) in methanol. The purification was accompanied by four reprecipitations from tetrahydrofuran and methanol. The characterization of some prepared oligomers was shown as follows:

ABATQ - 1, 97.3% yield.

NMR ($CDCl_3$) δ 1.73 (d, 5H) [6H], 2.60 (s, 1H) [1H], 7.0-8.5 (m, 29H) [26.5H] : the theoretical value was shown in [].

Anal. Calcd. for $C_{96}H_{67}N_8O_4$: C, 82.59; H, 4.80; N, 8.03

Found: C, 81.13; H, 4.72; N, 9.66

ABATQ - 2, 100% yield.

NMR ($CDCl_3$), δ 1.73 (d, 6H) [6H], 2.20 (s, 1H) [1H], 7.0-8.5 (m, 32H) [29H].

Anal. Calcd. for $C_{102}H_{71}N_8O_4$: C, 83.22; H, 4.82; N, 7.61

Found: C, 79.84; H, 4.63; N, 8.65

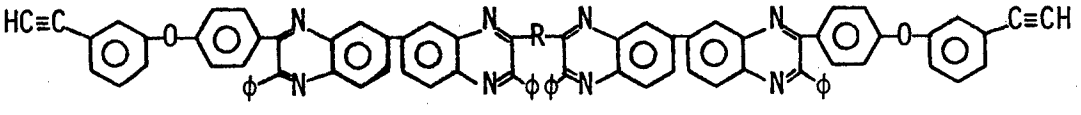
ABATQ - 3, 100% yield.

NMR ($CDCl_3$), δ 1.73 (d, 6H) [6H], 2.20 (s, 1H) [1H], 7.0-8.5 (m, 31H) [29H].

Anal. Calcd. for $C_{102}H_{71}N_8O_5$: C, 82.32; H, 4.77; N, 7.53

Found: C, 80.06; H, 4.33; N, 7.60

Acetylene terminated quinoxaline oligomer. The various structures prepared are shown in Figure 2.



ATQ

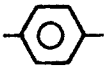
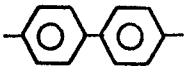
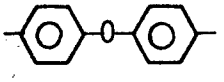
Oligomer	R
ATQ - 1	
ATQ - 2	
ATQ - 3	

FIGURE 2. Structures of ATQ series oligomers

General Preparation

Acetone adduct of acetylene terminated quinoxaline oligomer (ABATQ series, 4.80 g) and sodium hydroxide (2.0 g) were mixed with 1,4-dioxane (70 ml). The reaction mixture was refluxed for 20 hr. The resulting mixture was poured into 400 ml of methanol. After filtration of precipitate, the purification was accomplished by three reprecipitations from tetrahydrofuran and methanol. The characterization of some prepared oligomers was shown as follows:

ATQ - 1

NMR ($CDCl_3$), δ 3.0 (s, 1H) [1H], 7.0-8.5 (m, 34H) [26.5H]

Anal. Calcd. for $C_{90}H_{55}N_8O_2$: C, 84.45; H, 4.30; N, 8.76

Found: C, 82.45; H, 4.47; N, 9.84

ATQ - 2

NMR ($CDCl_3$), δ 3.0 (s, 1H) [1H], 7.0-8.5 (m, 32H) [29H]

Anal. Calcd. for $C_{96}H_{59}N_8O_2$: C, 85.02; H, 4.35; N, 8.27

Found: C, 81.04; H, 4.24; N, 8.93

ATQ - 3

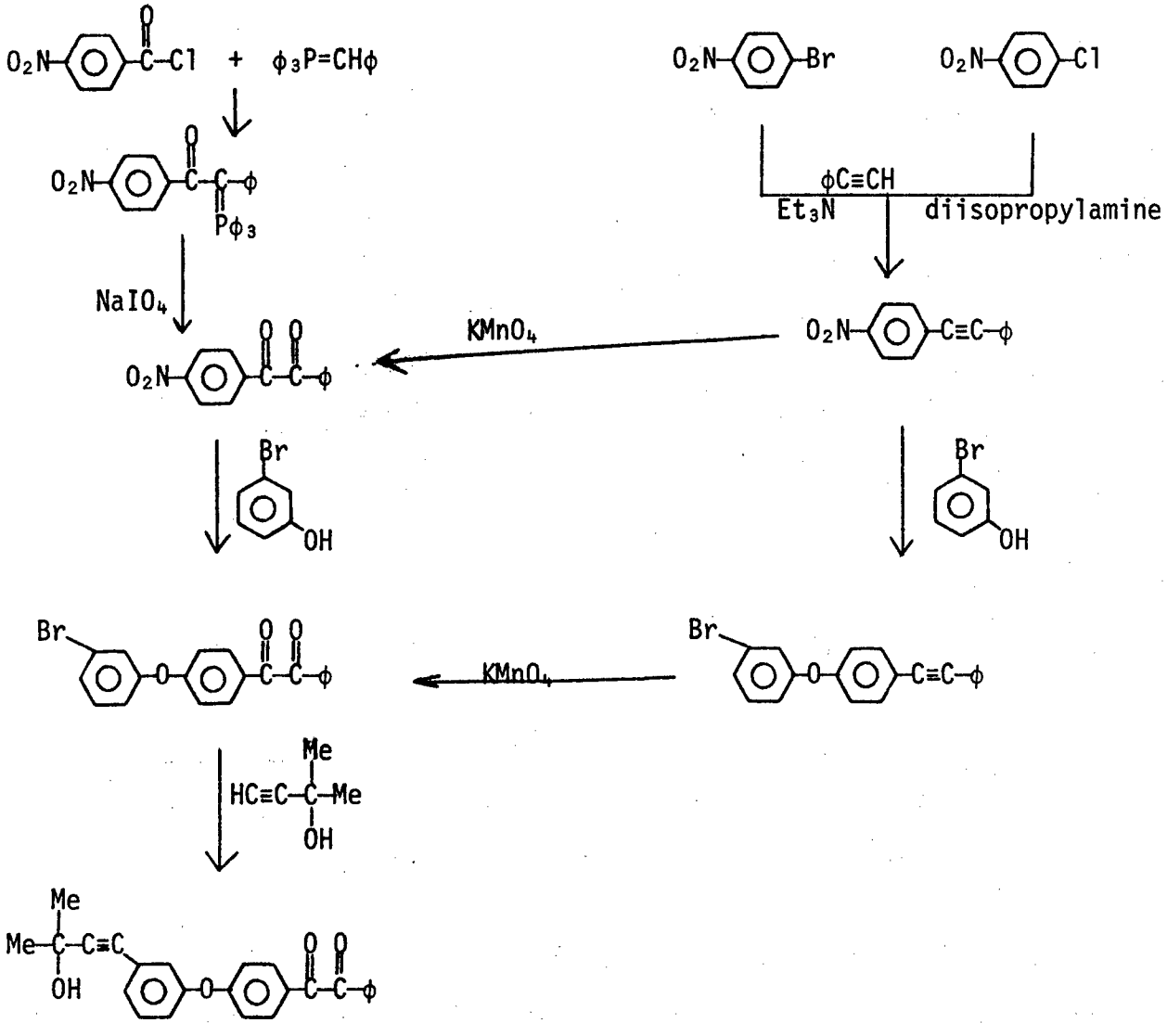
NMR ($CDCl_3$), δ 3.0 (s, 1H) [1H], 7.0-8.5 (m, 32H) [29H]

Anal. Calcd. for $C_{96}H_{59}N_8O_3$: C, 84.03; H, 4.30; N, 8.17

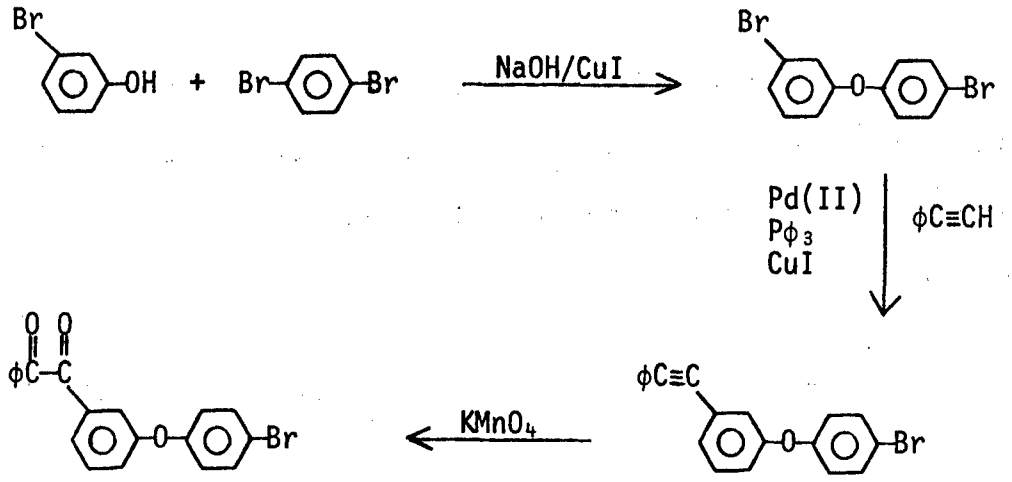
Found: C, 78.58; H, 4.13; N, 8.25.

Synthesis of 4-(3-bromophenoxy)benzil. H. M. Relles et al. have reported the new method of bis benzils prepared by nucleophilic aromatic nitro displacement reaction.[3] In this work, 4-(3-bromophenoxy)-benzil was prepared by using the same method in aprotic solvent. Table I shows the reaction conditions and results. In these reaction conditions, a relatively rapid nitro displacement reaction proceeded to give the benzil

in very high yield. Elemental analysis, infrared spectra, and observed ^{13}C-NMR chemical shifts were agreed well with the structure of this compound. This m-bromo compound had lower m.p. than the p-bromo one (3-(4-bromophenoxy)benzil).



SCHEME I



SCHEME II

TABLE I

Synthesis result of 4-(3-bromophenoxy)benzil

Exp.	Solvent	Temp. (^{o}C)	Time (hr)	Yield (%)
BB - 1	DMSO	100	48	85.1
BB - 2	DMSO	120	24	53.5
BB - 3	DMF	120	30	61.9
BB - 4	DMF	25	72	91.3

m-bromophenol (0.055 mol), p-nitrobenzil (0.05 mol), and K_2CO_3 (0.11 mol) in aprotic solvent (250 ml) under nitrogen.

Synthesis of 3-(4-bromophenoxy)benzil. At first, we had an intention in which 3-(4-bromophenoxy)benzil was synthesized from another route by using (3,4'-dibromo)diphenyl ether as an intermediate (see Scheme II). However, (3-phenylethynyl-4'-bromo)diphenyl ether was obtained predominantly in the reaction of phenylacetylene with (3,4'-dibromo)diphenyl ether. It

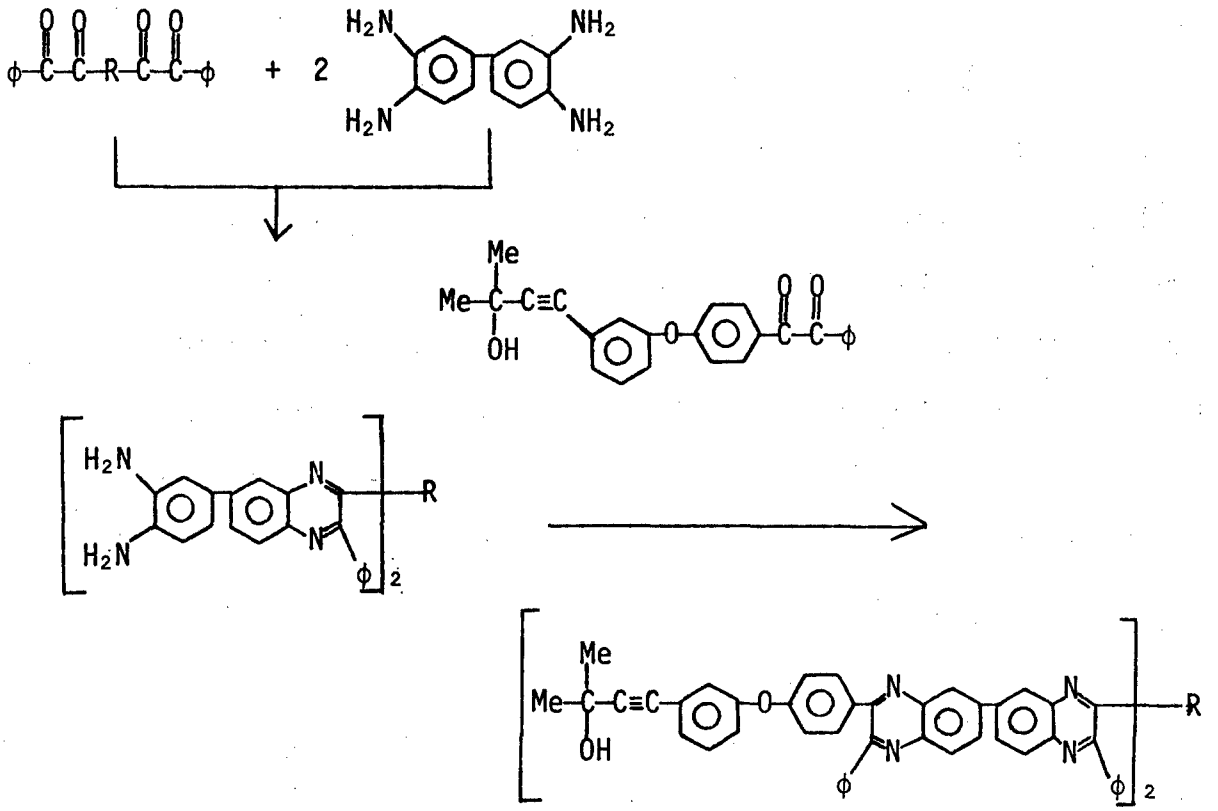
was shown from this phenylacetylation that m-bromine group had higher reactivity than p-bromine group. 3-(4-Bromophenoxy)benzil was prepared almost quantitatively by the oxidation reaction of (3-phenylethynyl-4'-bromo)diphenyl ether. TLC spot of this compound showed the different position to that of 4-(3-bromophenoxy)benzil. Elemental analysis and infrared spectra were agreed well with the structure of this compound.

Synthesis of 4-nitrodiphenylacetylene. Since H. A. Dieck and F. R. Heck reported palladium catalyzed synthesis of aryl, heterocyclic, or vinylic acetylene derivatives,[4] this reaction has made use of a good method for benzils by oxidizing arylacetylenes.[1] Phenylacetylation of 1-bromo-4-nitrobenzene in triethylamine gave a high yield of pure 4-nitrodiphenylacetylene. However, this reaction has not almost occurred in triethylamine in the case of 1-chloro-4-nitrobenzene. The alkyl acetylene was considered to be more reactive when more basic secondary amines were employed rather than triethylamine. As a result, phenylacetylation from 1-chloro-4-nitrobenzene in diisopropylamine gave 43% yield of pure material (see Scheme I).

Synthesis of acetone adduct of EPB and its hydrolytic displacement of acetone. This compound was obtained in high yield by using same method as synthesis of 4-nitrodiphenylacetylene. An attractive method[5] reported in 1979 involved the reaction of an aryl bromide with 2-methyl-3-butyn-2-ol using dichloro-bis(triphenylphosphine)palladium/cuprous iodide catalyst followed by cleavage of the intermediate with sodium hydroxide. This route, however, was inappropriate to prepare the desired ethynyl α-diketones since α-diketones undergo cleavage and rearrangement in the presence of a strong

base. A variation of this route employed the use of trimethylsilyl acetylene instead of 2-methyl-3-butyn-2-ol. The trimethylsilyl group can be cleaved from the intermediate with a weak base without harming the α-diketone. In this work, we tried other bases, but potassium t-butoxide and lithium t-butoxide gave unsatisfactory results.

Synthesis of acetone adduct of acetylene terminated quinoxaline oligomer and its hydrolytic displacement of acetone.

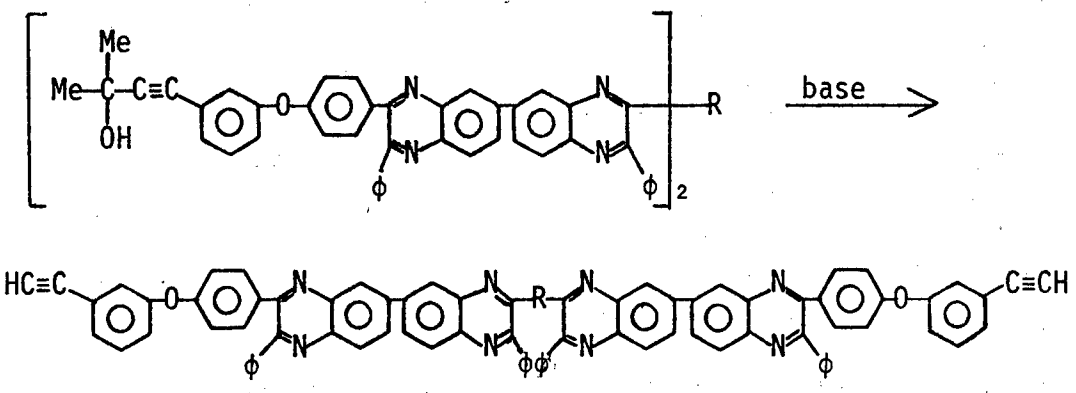


SCHEME III

Every formation reaction (Scheme III) of quinoxaline oligomers occurred quantitatively. The observed intensities of ^{1}H-NMR peaks agreed well with the structures of these oligomers. Infrared spectra showed the characteristic absorptions of ν_{CH} of methyl (2985 cm^{-1}) and $\nu_{C\equiv C}$ (2200 cm^{-1})

in addition to the disappearance of $\nu_{C=O}$ (1730 dm^{-1}). All the oligomers prepared were soluble (about 20%) in organic solvents such as methylene chloride, chloroform, 1,4-dioxane, tetrahydrofuran, and DMF.

Next, we tried to examine the hydrolytic displacement of acetone of these oligomers (Scheme IV).



SCHEME IV

Table II shows the reaction conditions and results for some acetone adduct of acetylene terminated quinoxaline oligomers. Conversion of the secondary acetylenes to primary acetylenes was carried out effectively by hydrolytic displacement of acetone with sodium hydroxide in dioxane or DMF in comparison with chloroform and THF as solvents. These solvents have relatively high boiling points and dissolve some amount of quinoxaline oligomer. ^{1}H-NMR spectra of these oligomers showed the peak of acetylene proton (–C≡CH) at δ 3.0 position, and peaks of $-CH_3$ and –OH disappeared. Infrared spectra showed the characteristic absorption of $\nu_{C\equiv CH}$ (3290 cm^{-1}). The observed intensities of the peaks in the ^{1}H-NMR spectra agreed with the structures of these oligomers.

TABLE II

Summary of Hydrolytic Displacement of Acetone of Some Oligomers

Starting Material	Solvent	Reaction Temp. (°C)	Time (hr)	Degree* of Hydrolytic Displacement of Acetone (%)
ABATQ - 1	dioxane	101	4	100
	DMF	100	4	100
	$CHCl_3$	61	16	---
ABATQ - 2	dioxane	101	5	100
	DMF	100	4-16	55-100
ABATQ - 3	dioxane	101	12	100
	DMF	100	5	95
	THF	66	5	85

ABATQ, 4.80 g; NaOH, 2.0 g; solvent, 70 ml

*Calculated from the intensity of proton peaks in ^{1}H-NMR spectra.

Acetone adduct of 3-(4-ethynylphenoxy)benzil. 3-(4-Bromophenoxy)-benzil (6.00 g, 15.7 mmol), 2-methyl-3-butyn-2-ol (2.65 g, 31.5 mmol), palladium diacetate (0.010 g), triphenylphosphine (0.204 g), copper iodide (0.041 g), and triethylamine (60 ml) were stirred at reflux temperature for 16 hr under nitrogen.

After cooling to room temperature, the resulting mixture was poured into a mixture of chloroform (400 ml) and 10% HCl (500 ml). After separation of organic layer, chloroform was removed by evaporation. The crude was dissolved in 200 ml of ether and washed with 5% HCl (600 ml), water (200 ml x 3), and saturated NaCl (600 ml). After evaporating of ether, the crude was purified by column chromatography (silica gel 40-140 Mesh, benzene as eluent). Pure material (4.68 g, 77.6%) was obtained as a dark gum.

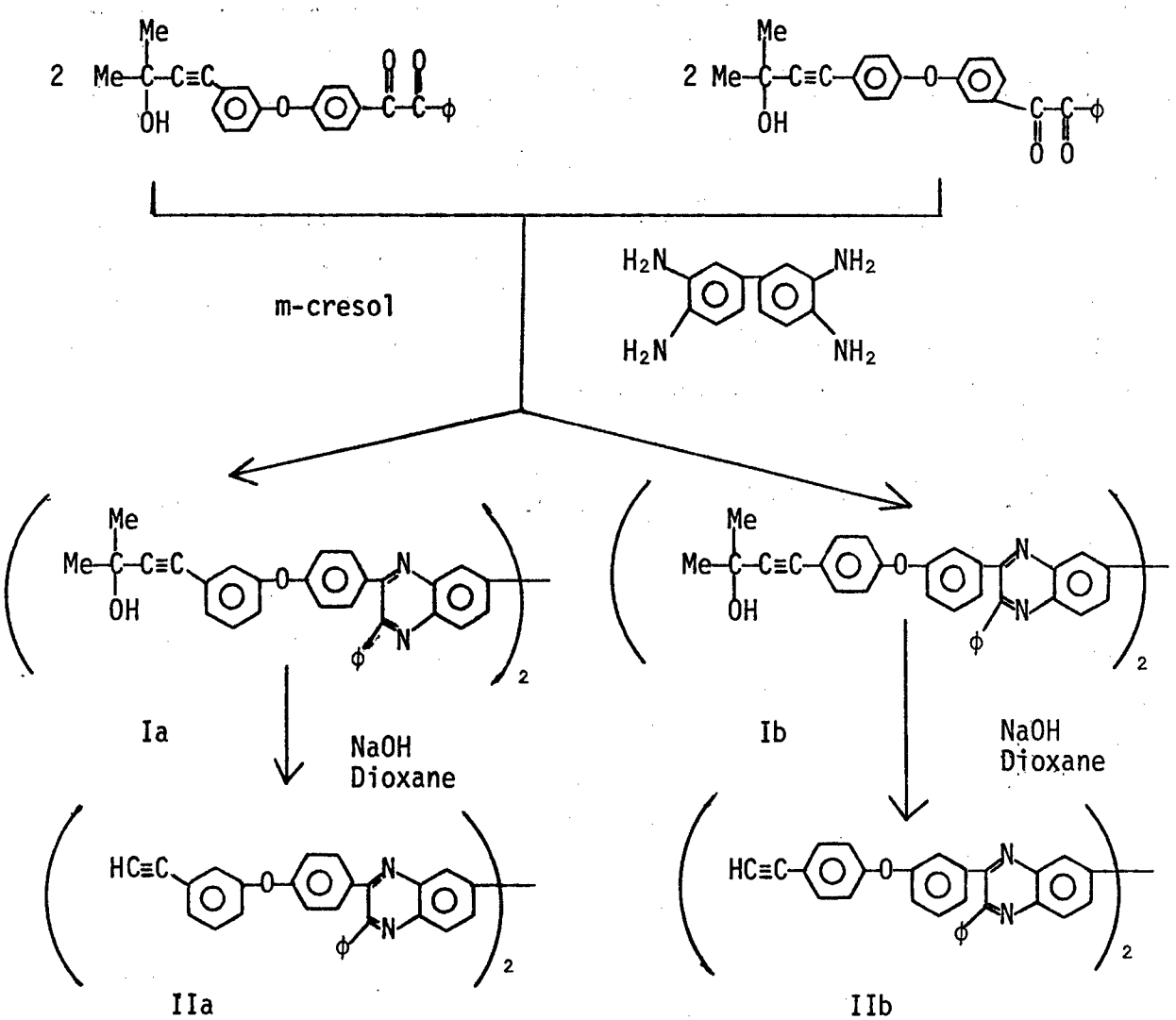
^{1}H-NMR ($CDCl_3$) δ 1.17 (d, 6H), 2.0 (s, 1H), 6.8-8.0 (m, 13H)

Anal. Calcd. for $C_{25}H_{20}O_4$: C, 78.14; H, 5.20

Found: C. 78.02; H, 5.33

The preparation methods of model compounds (acetylene terminated quinoxalines) are shown in Scheme V.

Model compounds Ia and Ib. 3,3'-Diaminobenzidine (0.857 g, 4 mmol) was dissolved in 42 ml of m-cresol. The solution of acetone adduct of 4-(3-ethynylphenoxy)benzil (or 3-(4-ethynylphenoxy)benzil) in chloroform (10 ml) was added into it and chloroform was removed by distillation. The resulting mixture was stirred at 90-100°C in an oil bath for 16 hr under nitrogen. Then, the mixture was precipitated into a solution of 10% NaOH (26 g) in methanol. The purification was carried out by two precipitations from tetrahydrofuran and methanol. The yield was almost quantitative (green solid).



SCHEME V

Model compounds IIa and IIb. Ia or Ib (1.00 g) and sodium hydroxide (0.6 g) were mixed with 70 ml of 1,4-dioxane. The mixture was refluxed for 24 hr. Then, this solution was poured into methanol. The purification was carried out by two precipitations from tegrahydrofuran and methanol.

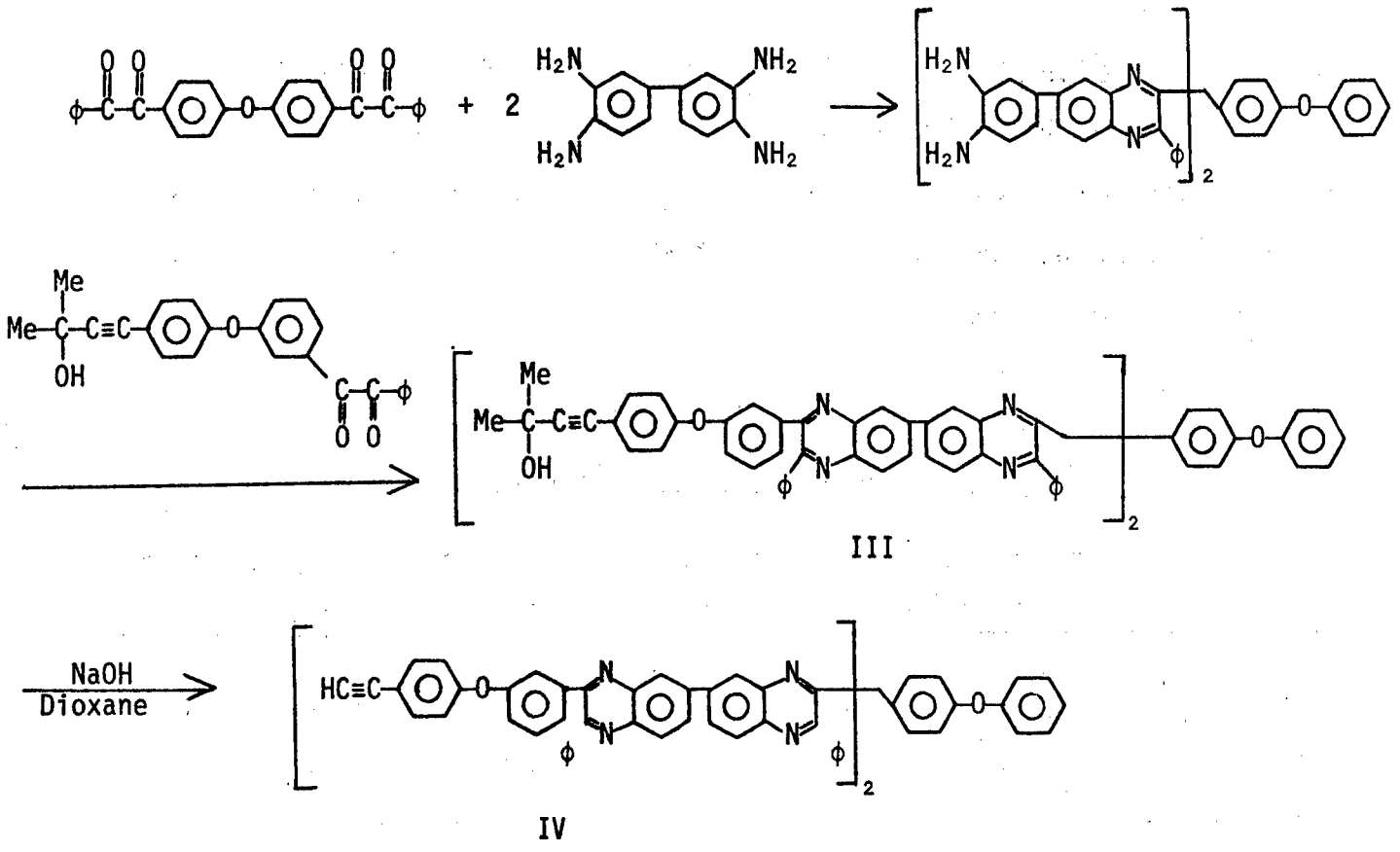
TABLE III

Characterization of Model Compounds

Compound	Formula	Intensity of ^{1}H-NMR ($CDCl_3$) peaks			Elemental Analysis C	N	N (%)
		ArH	OH	CH_3			
Ia	$C_{62}H_{46}N_4O_4$	δ 6.7-8.6	2.2	1.6	79.38	4.85	5.98
		20.1	1	6.0			
Ib		21.7	1	5.5	77.11	4.93	7.53
		(16	1	6)	(81.73	5.10	6.15)
		ArH		C≡CH			
IIa	$C_{56}H_{34}N_4O_2$	δ 6.7-8.6		3.1	74.02	4.09	6.24
		18		1			
IIb		25		1	75.15	4.21	7.62
		(16		1)	(84.60	4.32	7.05)

Theoretical values are shown in parenthesis.

Acetylene terminated quinoxaline oligomer. The preparation of the oligomer is shown in Scheme VI.



III

IV

SCHEME VI

Oligomer III. 3,3'-Diaminobenzidine (0.857 g, 4.0 mmol) was dissolved in 20 ml of m-cresol in 100 ml flask equipped with a mechanical stirrer. The flask was suspended in a 90-100°C oil bath under nitrogen. The solution of 4,4'-bis(phenylglyoxaloyl)diphenyl ether (0.868 g, 2.0 mmol) in m-cresol (15 ml) was added into it, and the reaction mixture was stirred for 6 hr in a 90-100°C oil bath under nitrogen. Then, the solution of acetone adduct of 3-(4-ethynylphenoxy)benzil in chloroform (10 ml) was added. The chloroform was removed by distillation, and the reaction mixture was heated for 6 hr at 90-100°C followed by precipitation into a solution of 10% sodium hydroxide (sufficient quantity to neutralize the m-cresol) in methanol. Purification was accomplished by two precipitations from tetrahydrofuran and methanol.

Oligomer IV. Oligomer III (2.0 g) and sodium hydroxide (0.85 g) were mixed with 40 ml of dioxane in 100 ml flask equipped with a magnetic stirrer. The reaction mixture was refluxed for 24 hr. The mixture was poured into methanol and filtered. Purification was accomplished by two reprecipitations from tetrahydrofuran and methanol.

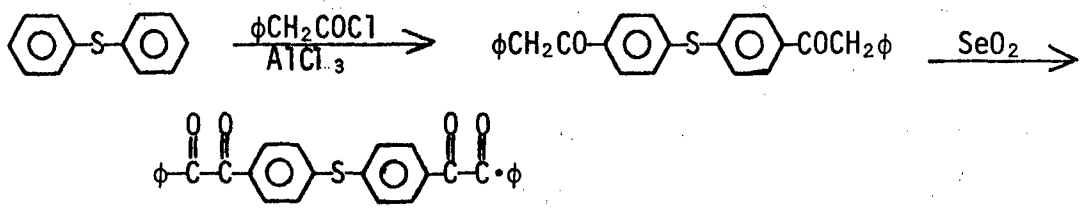
TABLE IV

Characterization of Oligomers

Oligomer	Formula	Intensity of ^{1}H-NMR ($CDCl_3$) peaks			Elemental Analysis C	H	N (%)
		ArH	OH	CH_3			
III	$C_{102}H_{71}N_8O_5$	δ 6.9-8.6	2.2	1.7	76.39	4.21	9.13
		62	1	6			
		(29	1	6)	(82.32	4.77	7.53)
		ArH		-C=CH			
IV	$C_{96}H_{59}N_8O_3$	δ 6.9-8.6		3.1	78.00	3.59	8.18
		31		1			
		(29		1)	(84.03	4.30	8.17

Theoretical values are shown in parenthesis.

The preparation method of 4-phenylglyoxaloylphenyl sulfide is shown in Scheme VII.



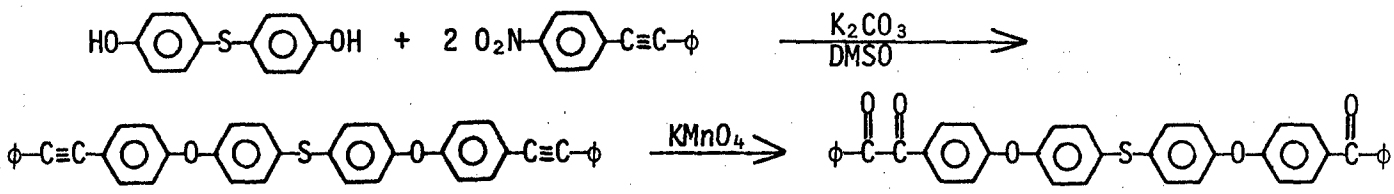
SCHEME VII

p-Phenacetylphenyl sulfide. This compound was prepared according to known procedures.[7] To a stirred mixture of anhydrous aluminum chloride (32 g, 0.24 mol) and carbon disulfide (100 ml) cooled by an ice bath was added a mixture of phenyl sulfide (18.6 g, 0.10 mol) and phenylacetyl chloride (32.0 ml, 0.24 mol) over 1 hr. The reaction mixture was stirred for 1 additional hour at room temperature, and was then refluxed for 1.5 hr. The carbon disulfide was distilled from the mixture, and the remaining solid was washed with ice water containing HCl (50 g). The filtrate was dissolved in 400 ml of hot chlorobenzene. Filtering the cooled solution, slurrying the collected crystals with pentane, filtering again, and drying gave a crude product. The crude was recrystallized from pyridine to afford 32.9 g (77.8%) of pure material as white solid, m.p. 194-195°C (lit. 198.5-199.5°C[7] and 194-196°C[8]).

^{1}H-NMR (DMSO-d_6) δ 4.4 (s, 4H), 7.3-8.2 (m, 18H)

4-Phenylglyoxaloylphenyl sulfide. p-Phenacetylphenyl sulfide (16.92 g, 0.04 mol), selenium dioxide (15.54 g, 0.14 mol), and acetic anhydride (400 ml) were refluxed for 5 hr. After cooling to room temperature, the selenium metal was filtered off and the precipitate was washed with a few ml of acetic anhydride. The filtrate was stirred with 400 ml of warm water. Upon cooling, a solid was separated and purified by column chromatography (alumina, benzene as eluent). After concentration of the eluate to 75 ml followed by cooling in ice water, pentane (150 ml) was added into this solution. After filtration, the crude was recrystallized from hexane to afford 9.14 g (51.2%) of pure material as dark crystal. m.p. 81-83°C (lit.[7] 90.0-91.6°C).

The preparation method of 4,4'-bis(phenylglyoxaloylphenoxy)diphenyl sulfide is shown in Scheme VIII.

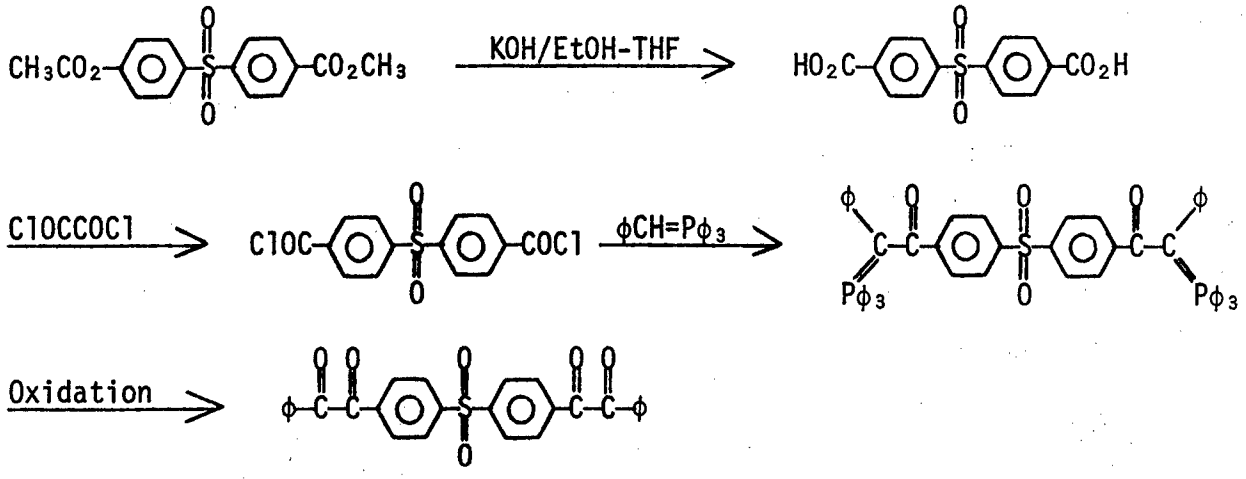


SCHEME VIII

4,4'-Bis(phenylethynylphenoxy)diphenyl sulfide. 4,4'-Thiodiphenol (3.27 g, 0.015 mol), 4-nitrodiphenylacetylene (6.70 g, 0.030 mol), and potassium carbonate (anhydrous granular 10.33 g, 0.075 mol) were mixed with 35 ml of DMSO. This reaction mixture was stirred in an 80°C oil bath for 30 hr under nitrogen. After cooling to room temperature, the resulting mixture was poured into a mixture of chloroform (200 ml) and 10% HCl (800 ml). The organic layer was extracted with six successive 50 ml portions of dilute HCl, and washed with water, 5% KOH (800 ml) and 10% NH_4Cl (600 ml). The resulting solution was dried over $MgSO_4$. After evaporation of the chloroform, the crude was purified by column chromatography (silica gel, 40-140 Mesh, methylene chloride as eluent). Pure compound (6.63 g, 77.5%) was obtained as a yellow solid; m.p. 85.5-88°C.

4,4'-Bis(phenylglyoxaloylphenoxy)diphenyl sulfide. 4,4'-Bis(phenylethynylphenoxy)diphenyl sulfide (5.71 g, 0.01 mol) was dissolved in 100 ml of methylene chloride. The flask was suspended in an oil bath maintained at 45°C. Adogen-464 (0.68 g) was added along with glacial acetic acid (6.68 ml). Potassium permanganate (6.32 g, 0.04 mol) was added through the condenser and rinsed down with 100 ml of water. The reaction mixture was refluxed for 18 hr and worked up as described before for preparation of 1,4-bis(phenylglyoxaloyl)-benzene.[1] The crude solid was purified by column chromatography (silica gel, 40-140 Mesh, benzene as eluent). Pure material (4.50 g, 71.0%) was obtained as an orange gum.

We tried to prepare 4,4'-bis(phenylglyoxaloyl)phenyl sulfone from Scheme IX.



SCHEME IX

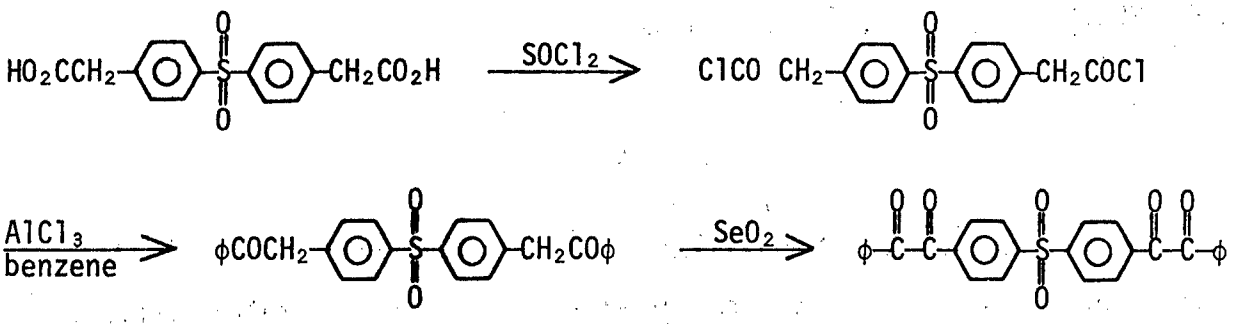
4,4'-Sulfonyldibenzoic acid. 4,4'-Sulfonylbis(methylbenzoate) (42.8 g, 0.128 mol) was mixed with hot ethanol (600 ml) and tetrahydrofuran (200 ml). Potassium hydroxide (40 g) was added carefully, and the solution was refluxed for 24 hr.

After cooling to room temperature, the solid was collected by filtration and dissolved in water. Hydrochloric acid was added until the solution was acidic. The precipitate was collected by filtration. The crude was recrystallized from ethanol-tetrahydrofuran to afford 29.8 g (76.1%) of pure material as white solid; m.p. 375-378°C (lit.[9] 370-372°C).

Diphenyl sulfone-4,4'-dicarbonyl dichloride. 4,4'-Sulfonyldibenzoic acid (13.48 g, 44 mmol) was added to dry benzene (210 ml) and pyridine (21 ml) in a flask equipped with a mechanical stirrer. Oxalyl chloride (98 ml, 1.12 mol) was added slowly and very carefully. The mixture was stirred for 1 hr under nitrogen at room temperature. The temperature was then raised to 76-78°C for 6 hr. After cooling to room temperature, the solution was filtered and all volatiles removed by evaporation. The residue was almost nothing. Final compound could not be obtained under this reaction condition.

Bis-Benzils

4,4'-Bis(phenylglyoxaloylphenoxy)diphenyl sulfide showed lower melting point (gum) in comparison with 4-phenylglyoxaloylphenyl sulfide, because of having ether bond in molecule. 4,4'-Bis(phenylglyoxaloyl)-phenyl sulfone could not be prepared from Scheme IX. W. Wrasidlo, et al.[10] prepared this compound from the following scheme:



SCHEME X

Another route is considered to prepare 4,4'-bis(phenylglyoxaloyl)-phenyl sulfone. This is to say, p-phenacetylphenyl sulfone is prepared from the reaction of phenyl sulfone with phenylacetyl chloride under aluminum chloride as a catalyst. Next, the oxidation of p-phenacetylphenyl sulfone is carried out by using selenium dioxide as oxidizing agent.

Model Compounds and Oligomer

Acetone adduct of acetylene-terminated quinoxaline model compounds (Ia and IIa) and oligomer (III) were obtained almost quantitatively. Infrared spectra of these materials showed the characteristic absorptions at 3050 cm^{-1} (ν_{OH}) and 2985 cm^{-1} (ν_{CH} of methyl). On the other hand, the absorption of $\nu_{C=O}$ (1730 cm^{-1}) disappeared in chart. Data of ^{1}H-NMR and elemental analysis also supported these structures.

After hydrolytic displacement of acetone with sodium hydroxide in 1,4-dioxane, infrared spectra of model compounds (Ib and IIb) and oligomer

(IV) showed the characteristic absorption at 3290 cm^{-1} ($\nu_{C\equiv CH}$): Proton signals of OH (δ 2.2) and CH_3 (δ 1.6) disappeared in ^{1}H-NMR spectra.

The thermal behavior of acetylene-terminated quinoxaline model compounds and oligomers was studied by differential scanning calorimetry (DSC). The thermal properties of model compound (IIa) and oligomer BATQ-0* was reported in a previous paper.[11]

*BATQ-0

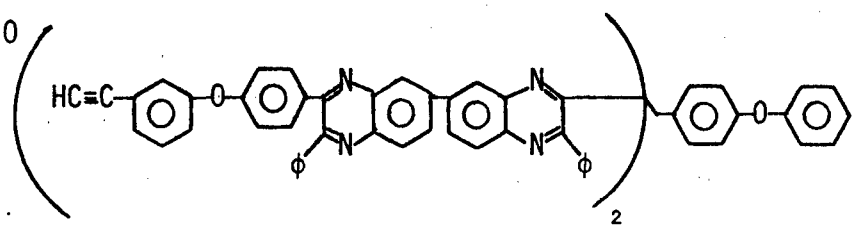
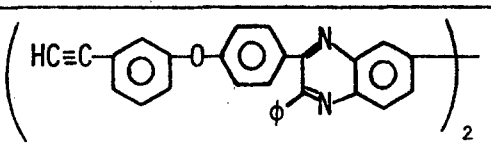
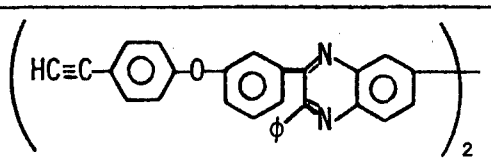
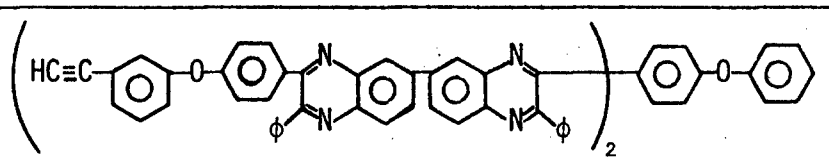
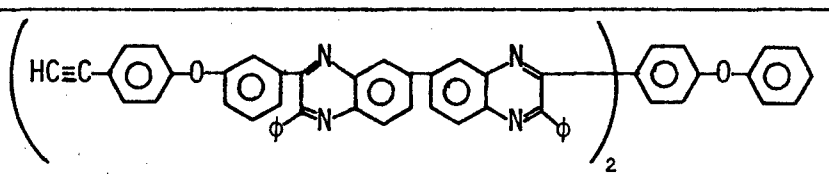


TABLE V

Characterization of Model Compounds and Oligomers

Compound No.	Structure	Tg*
IIa		119°C (lit. 120-130°C
IIb		82°C
BATQ-0		171°C
IV		131°C

*Determined by DSC at 10°C per min. under nitrogen

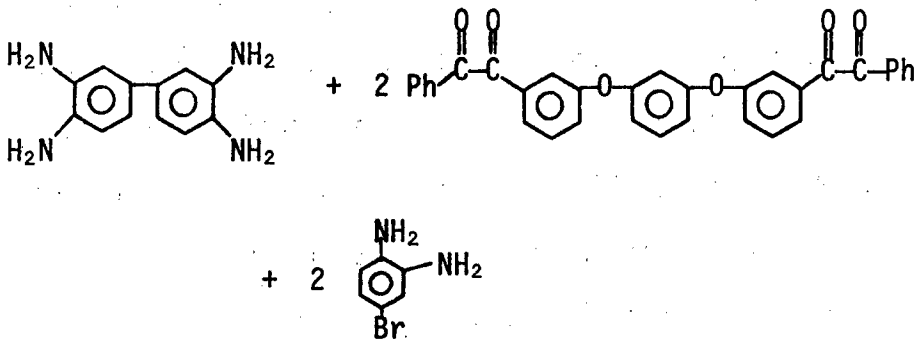
Preparation of m-bis(phenylethynyl-m-phenoxy)benzene. A mixture of m-bis(bromo-m-phenoxy)benzene (5.69 g, 13.5 mmol),[12] triphenyl phosphine (273 mg), copper iodide (55 mg), and palladium acetate (14 mg) in dry triethylamine (50 ml) was stirred and heated at 100°C (bath). After 10 min, phenylacetylene (2.77 g, 27.1 mmol) was added through the condenser. Phenylacetylene was rinsed into the reaction mixture with triethylamine (5 ml) and the reaction mixture was refluxed overnight (15 hr). After cooling to room temperature, the suspension was filtered and the solid was washed thoroughly with anhydrous ether. Filtrate and washings were combined and concentrated using rotavapor. Water (100 ml) was added to the residue. Extraction with ether was carried out (3 x 50 ml). The combined ether extracts were washed with water and brine, and dried over anhydrous sodium sulfate. Removal of ether gave a viscous residue which slowly solidified to pale yellow mass (6 g). TLC examination showed several spots consisting, however, of one major component. As purification by column chromatography was not possible, this product was used directly in the next step.

Potassium permanganate oxidation of m-bis(phenylethynyl-m-phenoxy)-benzene to the corresponding bis benzil. m-Bis(phenylethynyl-m-phenoxy)-benzene (6 g, 13.0 mmol) was dissolved in dichloromethane (200 ml), and transferred to a 500 ml three-necked flask equipped with a mechanical stirrer. The flask was surrounded by an oil bath maintained at 45°C. Adogen-464 (1.44 g) was added followed by glacial acetic acid (15 ml). Potassium permanganate (10.3 g, 6.5 mmol) was added through the condenser and rinsed down with water (140 ml). The mixture was refluxed for 6 hr with vigorous stirring.

After cooling, excess permanganate was reduced by cautiously adding solid sodium bisulfite. When the purple color was discharged, the reaction mixture was acidified with conc. hydrochloric acid. Organic layer was separated

and aqueous phase was extracted once with dichloromethane (50 ml). The combined organic layer was washed with saturated aqueous sodium bicarbonate and with water. After drying over anhydrous sodium sulfate, dichloromethane was removed under reduced pressure to give a viscous yellow-colored liquid. TLC examination revealed one major compound. This was isolated by chromatography on a silica gel column. Bis benzil (4.9 g) was obtained in ~ 90% purity.

Preparation of oligomers derived from



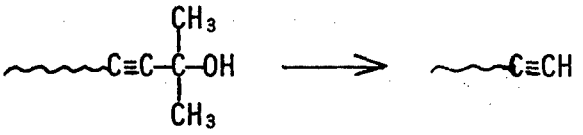
A solution of bis benzil (3.99 g, 7.6 mmol) in m-cresol (35 ml) was stirred and heated at 110°C (bath). A solution of 3,3'-diaminobenzidine (812 mg, 3.8 mmol; note -- Celanese DAB was used without purification) in m-cresol (30 ml) was added dropwise to the bis benzil solution over a period of 50 min. An additional 10 ml of m-cresol was used to rinse the addition-funnel and this was added over 5 min. Reaction mixture was stirred and heated for 3 hr. Solid bromodiamine (1.42 g, 7.6 mmol) was added in one lot, and stirring and heating continued for 3 hr. After cooling, reaction mixture was poured into methanolic sodium hydroxide solution (250 ml of 20% NaOH in 350 ml of methanol). The precipitated solid was filtered, washed with methanol, and dried (5.4 g). This was subsequently purified by two precipitations from tetrahydrofuran and methanol; 3.2 g, m.p. 185-187°C (softening around 180°C).

Ethynylation of the above dibromoquinoxaline oligomeric mixture.

A mixture of dibromoquinoxaline oligomeric mixture (4.32 g), triphenylphosphine (546 mg), copper iodide (109 mg), palladium acetate (27 mg) in dry pyridine (50 ml) was stirred and heated (bath temp. 110-116°C). After few minutes, freshly distilled 2-methyl-3-butyn-2-ol (1.45 g, 17.2 mmol) was added through the condenser and rinsed down with pyridine (5 ml). After heating and stirring overnight (21 hr), the cooled reaction mixture was poured into methanol (800 ml). The solid was filtered, washed with water and methanol. As there was only very little incorporation (by NMR) of the acetylenic moiety viz., 2-methyl-3-butyn-2-ol, ethynylation step was repeated on the above solid using the same quantities of reagents as above. This time, however, bath temperature was raised to 130-132°C. After 24 hr of reflux (note -- ethynylation was complete at this stage because further reflux does not improve incorporation of acetylenic moiety (by NMR)), reaction was worked up as before. 3.97 g of a solid was obtained.

Anal. Calcd. for $C_{102}H_{70}N_8O_2$: C, 85.08; H, 4.91; N, 7.78

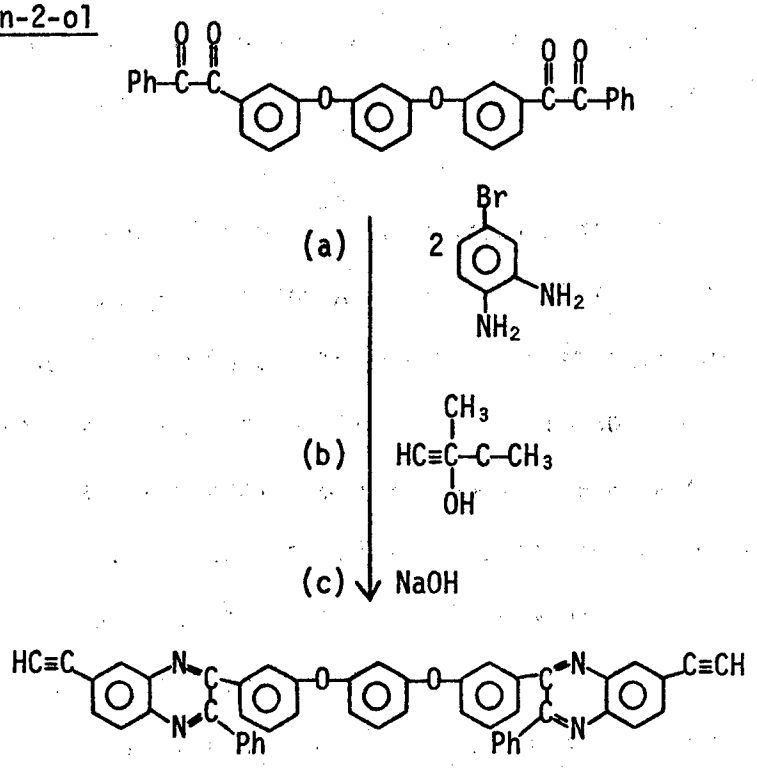
Found: C, 75.78; H, 3.94; N, 7.82

Deprotection step 

Product obtained in the previous step (3.37 g) was dissolved in AR $CHCl_3$ (110 ml). Ethylenediamine (10 ml) was added. After heating at 64°C (bath) for 2 hr, reaction mixture was cooled and washed with distilled water till free of ethylenediamine. Drying the chloroform layer over anhydrous sodium sulfate and subsequent removal of chloroform gave a brown solid (3.1 g). This solid was dissolved in dioxane (75 ml). Powdered sodium hydroxide (1 g) was added followed by water (5 ml). The reaction mixture was stirred while slowly

distilling off dioxane (110-115°, bath). When about 20 ml of dioxane remained to be distilled, more dioxane was added to the original volume. This process of addition of dioxane and its subsequent boil down was repeated 5 times. Reaction mixture was then filtered hot. Filtrate was collected and evaporated to a small volume (4-5 ml). Methanol (35 ml) was added. The precipitated solid was filtered, washed with methanol, and dried (1.6 g). This was purified by precipitation from tetrahydrofuran and methanol (1.1 g).

Reaction of bis benzil with bromophenylenediamine and 2-methyl-3-butyn-2-ol



a) Treatment of bis benzil with bromodiamine

A mixture of bis benzil (935 mg, 1.8 mmol) and bromodiamine (665 mg, 3.6 mmol) in m-cresol was refluxed (bath temp., 105-110°C) overnight (12 hr). After cooling to room temperature, reaction mixture was poured into methanolic sodium hydroxide (80 ml of 20% sodium hydroxide in 100 ml methanol). The solid was filtered, washed with methanol, and dried. It was purified once by

precipitation from tetrahydrofuran and methanol to give 600 mg of the product, m.p. ~ 114-118°C (softening around 110°C).

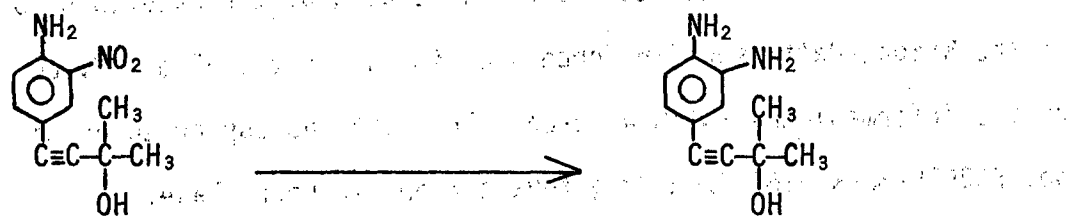
b) Ethynylation step

Product obtained in the previous step (600 mg) was dissolved in dry pyridine (10 ml). Triphenylphosphine (75.9 mg), copper iodide (20 mg), and palladium acetate (5 mg) were then added followed by 2-methyl-3-butyn-2-ol (467 mg, 5.6 mmol, large excess). Reaction mixture was stirred and refluxed at 130-136°C (bath) for 40 hr. Pyridine was removed under reduced pressure and the residue was dissolved in chloroform. Chloroform extract was washed with water. After drying over anhydrous sodium sulfate, solvent was removed to give dark solid product.

c) Deprotection step

Ethynylated product obtained above was dissolved in chloroform (25 ml), and ethylenediamine (1.5 ml) was added. After heating at 60°C (bath) for 2 hr, the reaction mixture was cooled and washed with water till free of ethylenediamine. Chloroform layer was dried over anhydrous sodium sulfate. Removal of chloroform gave a brown residue. This was dissolved in dioxane (50 ml). Powdered sodium hydroxide (250 mg) was added followed by addition of water (1 ml). Dioxane was slowly distilled off until about 15 ml remained. More dioxane was added to the original volume. This process of addition of dioxane and its subsequent boil down was repeated four times. The hot solution was filtered and the filtrate concentrated to a small volume (~ 2 ml). Methanol (15 ml) was added. The yellow solid that precipitated was filtered off (383 mg). This was purified by precipitation from tetrahydrofuran and methanol to give a yellow powdery solid (127 mg).

Sodium dithionite reduction of 4-(3'-nitro-4'-aminophenyl)-2-methyl-3-butyn-2-ol to the corresponding diamino compound.



A mixture of sodium dithionite (18.4 g, 106 mmol) and water (60 ml) was heated at 65° (temp. of reaction mixture) until solution was complete. Heating bath was removed, and aqueous sodium hydroxide (20 ml, 10% solution) was added immediately followed by addition of a solution of the nitro compound (580 mg, 2.6 mmol) in methanol (20 ml) (added in one lot). After stirring for 1/2 hr, the reaction mixture was saturated by the addition of solid sodium chloride. The resulting slurry was stirred with dichloromethane (50 ml) and filtered. The solid was washed twice with dichloromethane. Filtrate and washings were combined and dried over anhydrous sodium sulfate. Removal of the solvent gave an orange-brown solid, 10.43 g (85.8%), which was almost pure. Analytically pure sample was obtained by recrystallization from ethyl acetate-hexane as a pale orange crystal; m.p. 148-149°C; ^{1}H-NMR ($CDCl_3$ and DMSO-d_6) δ 1.50 (s, 6H), 1.98 (s, 1H), 2.80-4.20 (br s, 4H), 6.64 (dd, 2H), and 7.68 (s, 1H).

Anal. Calcd. for $C_{11}H_{14}N_2O$: C, 69.43; H, 7.43; N, 14.73

Found: C, 69.02; H, 7.22; N, 14.81

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12. This was prepared in 27% yield (F. E. Arnold, G. A. Loughran, B. A. Reinhardt, and E. J. Soloski, AFWAL-TR-81-4006 (1981)). Later the same compound was prepared in 75% yield by Hedberg and Hunsaker-Jubara by a modified procedure. (Personal communication from F. L. Hedberg and Marilyn Hunsaker-Jubara.)